

LEVEL

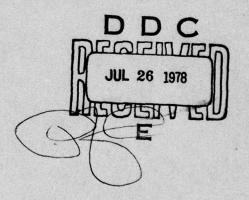
Effect of Hydrostatic Pressure on the Deformation Behavior of Polyethylene and Polycarbonate in Tension and in Compression



Final Report on Office of Naval Research Contract N00014-76-C-2005

W. A. Spitzig and O. Richmond

U. S. Steel Corporation Research Laboratory Monroeville, Pennsylvania 15146



Production in whole or in part is permitted for any purpose of the United States Government.

Distribution of this document is unlimited.

by

W. A. Spitzig and O. Richmond

Abstract

The stress-strain response of crystalline high density polyethylene and of amorphous polycarbonate has been determined in tension and in compression at superimposed pressures up to 1104 MPa (160 ksi). All tests were conducted at room temperature and at a single imposed strain rate, and the specimens were coated with silicone rubber to protect them from the pressurizing fluid. Strain softening occurred in the polycarbonate at low pressures but was inhibited by pressure. Tensile necking occurred in both materials, but was promoted by pressure in polyethylene and inhibited in polycarbonate.

The initial modulus, E, and the flow stress, σ , at a given offset strain varied linearly with the mean pressure, P, with essentially the same pressure coefficient, α . Thus $E = (1+\alpha P)E_0 \text{ and } \sigma = (1+\alpha P)\sigma_0, \text{ where } E_0 \text{ and } \sigma_0 \text{ are values at zero mean pressure.}$ In polyethylene, the coefficient, σ_0 , was the same in tension and compression, indicating that the strength differential between tension and compression was a simple manifestation of pressure-dependent yielding, as was

DISTRIBUTION STATEMENT A

Approved for public release; Distribution Unlimited

78 07 21 034

found previously for steels. In polycarbonate the coefficient, $\sigma_{_{\hbox{\scriptsize O}}}$, was different in tension and in compression, implying an effect due to the third stress invariant or to anisotropy.

Inelastic volume changes were determined from density and from dilatometer measurements. In polyethylene they were positive but much less than required by the normality flow rule of plasticity theory. This is consistent with earlier results on steels. In polycarbonate they were negative, in complete contrast to predictions of the normality flow rule.

The results suggest a constitutive model for polymers in which the flow stress is linearly dependent on mean pressure, but in which inelastic volume change is negligible, in agreement with earlier findings for steels. The results also suggest, however, that the pressure dependence of flow stress in polymers is the same as that of the initial modulus, which is not the case with steels.

BY DISTRIBUTION/AVAILABILITY CODES	JUSTIFICATION	NTIS DDC UNANNOUNC	White Section Buff Section
		JUSTIFICAT	
	Dist. AVAIL. 280/OF SPECIAL		

Introduction

Proposed yield criteria for polymers are generally based on pressure-modified versions of the Tresca or von Mises yield criteria, such as the Coulomb yield criterion 1,2,3) originally applied to soils. In general, the yield criteria used for metals, such as those of Tresca or von Mises, are not adequate for explaining the yield behavior of polymers because polymers are generally stronger in compression than in tension and show a large pressure dependence of yielding (see References 2 and 4-7 for a summary of most of the previous work). In both the Tresca and von Mises yield criteria, the yield and flow stresses in tension and in compression are identical and independent of hydrostatic pressure. However, recent studies on high-strength steels 8,9) have shown that these materials also have yield and flow stresses that are larger in compression than in tension and that are dependent on hydrostatic pressure. These results point out an inadequacy of the Tresca or von Mises yield criteria for describing the yield behavior in such materials, as well as in polymers and soils.

Analysis of the tension and compression results in the high-strength steels at atmospheric pressure and under hydrostatic pressures up to 1104 MPa (160 ksi), obtained in conjunction with determining the permanent volume expansions that occurred during plastic deformation, showed that the classical theory of plasticity

should be modified to include pressure-dependent yielding without requiring volume expansion. Such a theory has been proposed previously for the plastic deformation of soils and granular materials 10,11) and suggests the potential for a general plasticity theory applicable to a wide class of materials.

To explore the possibility of a generalized plasticity theory applicable to a wide range of materials, it was felt desirable to analyze the pressure dependency of the yield and flow behavior of the crystalline polymer polyethylene and the amorphous polymer polycarbonate. Previous work indicates a strong pressure dependency of the yield and flow stresses of polymers. 2,4,6,7) It also appears that a negligible permanent volume expansion results from plastic deformation of polymers, 12) as is observed in metals and granular materials.

A general deficiency in the previous work on polymers is the lack of a study in which pressure-dependent yielding in tension and in compression and volume changes resulting from plastic deformation were investigated on a given polymer. Because of the strong effect of specimen purity, crystallinity, and orientation of the specimen axis with respect to the draw direction, it is unrealistic to use results from different studies for the formulation of a basic theory. Also, recent studies have indicated that the pressure-transmitting fluid used in hydrostatic pressure studies can have an effect on the resultant properties

of some polymers, particularly on the ductility. 13-15)

Therefore, a meaningful analysis of the yield and flow criteria for polymers, for comparison with the previous results on steels, requires a systematic study in which all the important parameters are measured on the same polymer and care is taken to prevent any environmental effects from the pressure medium on the resultant properties.

tension and compression tests on polyethylene and polycarbonate at atmospheric pressure and at imposed pressure to 1104 MPa (160 ksi). The magnitudes by which the yield and flow stresses in compression exceed those in tension (strength-differential or S-D effect) and the permanent volume changes resulting from plastic deformation were determined for both polymers.

Materials and Procedures

Materials, Specimen Design, and Procedures

High-density polyethylene (950 kg/m³ or 59.3 lb/ft³) and Lexan polycarbonate were obtained as commercially extruded rods 25.4 mm (1 in.) in diameter. Various types of specimens were used throughout this study but all were machined directly from the extruded rods.

The specimens used to evaluate the effect of hydrostatic pressure on the yield and flow characteristics were designed to fit into the Harwood hydrostatic pressure unit. The tension specimens had threaded ends with a gage length of 25.4 mm and a gage diameter of 11.4 mm (0.45 in.), whereas the compression specimens were cylinders 25.4 mm high with a diameter of 12.7 mm (0.5 in.). At pressures of 828 and 1104 MPa (120 and 160 ksi) the polycarbonate specimens were reduced in gage length and in diameter because of the load limitation of the load cell and also because the tension specimens tended to fracture in the grip region. These tension specimens had a gage length of 23 mm (0.9 in.) and a diameter of 7.6 mm (0.3 in.), and the compression specimens were 19.0 mm (0.75 in.) high and had a diameter of 9.5 mm (0.375 in.).

Specimens tested in the hydrostatic pressure unit were coated with RTV silicone rubber, which required 24 hours at room temperature for curing. This coating did not bond to the polymers and was easily removed after testing. Tests at atmospheric pressure in air showed that the mechanical properties of the polymers were not affected by the coating. The same size tension and compression specimens were used to evaluate density changes resulting from plastic deformation at atmospheric pressure and at 828 MPa, and the same size compression specimens were used to evaluate the volume changes occurring during deformation at atmospheric pressure by testing in a dilatometer.

To obtain an accurate measure of the magnitude of the S-D effect of the two polymers at atmospheric pressure,

additional tension and compression tests were performed with a combined tension-compression specimen. 16) Both the gage length and the diameter of this specimen were 16.5 mm (0.65 in.) and a clip-on strain gage was used for strain measurements in both tension and compression tests. All tension and compression tests were conducted at a nominal strain rate of 7 x 10 4/sec. Volume-Change Measurements

Volume changes resulting from plastic deformation were determined from density measurements by using the apparatus and methods developed and described previously. 17) The only changes made were that the weighings in liquid were made in ethylene glycol monobutyl ether and kerosene for polyethylene and polycarbonate, respectively. The density measurements were made before and after straining the specimens. Any volume changes are those remaining after straining, that is, permanent volume changes, and not necessarily those that might have occurred during deformation. The grip ends of the tension specimens were removed after straining, and the final density determinations were made on the gage section. The amount of permanent strain of the specimens was measured during the final density measurements because some recovery occurred between the end of the test and the density determination (about 2 hours).

plastic deformation, compression specimens were deformed in a dilatometer containing mercury. The system used was similar to one described previously. The dilatometer, a specimen is deformed inside a cylinder containing mercury and the volume of mercury displaced from the cylinder as the specimen is deformed is measured by the height of the mercury column in a capillary tube connected with the cylinder. The displacement of the mercury column due to the motion of the ram itself is subtracted from the displacement resulting during deformation of a specimen to obtain the specimen volume change. The capillary system used is such that a 1 mm (0.04 in.) displacement of mercury corresponds to a relative volume change of the specimen of 0.025 percent.

Hydrostatic Pressure Tests

All the tension and compression tests under superimposed hydrostatic pressure were conducted in a Harwood hydrostatic pressure unit. This unit is also used for testing specimens at atmospheric pressure for comparison and for pressurizing specimens for subsequent testing at atmospheric pressure. The high-pressure unit is based on a previous design¹⁸⁾ and consists of a pressure cylinder and two separate hydraulic pressure systems. This arrangement permits independent movement of the two pressure rams and makes it possible to control both the pressure in the cylinder and the extension rate during a tension or compression test.

In tension testing, one end of the specimen is attached to the load cell and the other end to the lower ram, whereas for compression testing, the specimen is mounted in a compression cage which is attached to the load cell and the lower ram. For both tension and compression tests, straining of the specimen is accomplished by lowering the bottom ram.

Motion of the ram is controlled by a precision metering valve, and the amount of extension or contraction of a specimen is measured by an LVDT attached to the bottom ram outside the pressure cylinder. The pressure cylinder is filled with a solution of castor oil plus 20 percent methyl alcohol and pressure is generated by compressing the fluid with the upper ram.

The pressure generated in the cylinder is measured from a change in the electrical resistivity of a manganin coil located inside the cylinder. The pressure during a test is controlled within about one percent by controlling the upper ram movement during a test. To ensure constant pressure during a test, the upper ram is driven by the discharge from a precharged accumulator contained within the pressure system. A precision metering valve allows accurate control of the upper ram movement so that its movement is synchronized with that of the lower ram, thereby keeping the pressure in the chamber constant during a test.

The load cell used in the hydrostatic pressure unit is based on a previous design, ^{18,19)} and consists of two concentric cylinders containing strain gages. The outer cylinder contains the active strain gages and is subjected to the load, whereas the inner cylinder contains the strain gages that compensate for pressure and temperature effects. The load cell is calibrated under pressure by using a spring calibration technique ²⁰⁾ to account for the effect of hydrostatic pressure on the output of the load cell.

To determine reliable values for the initial modulus and the magnitude of the S-D effect under hydrostatic pressure, it is necessary to separate the machine displacements from those that the specimen undergoes. The limited space in the hydrostatic pressure unit precludes the use of a clip-on strain gage for strain measurement during testing. The LVDT measurements used to monitor ram motion include both the machine and specimen displacements.

To separate the machine displacements from the specimen displacements tension and compression tests were made, at each of the pressures studied, on steel specimens that only underwent small elastic displacements in the load range used for the polymers. These test results give the machine displacements throughout the load range used for the polymers and, thereby, can be subtracted from the total

displacements measured during a test to obtain the actual specimen displacements. 21) Using the procedure at atmospheric pressure on compression specimens tested in the hydrostatic-pressure unit resulted in initial moduli and offset yield and flow stresses in good agreement with the corresponding values obtained on specimens tested in air by using a clip-on strain gage. The values obtained for the initial moduli in tension tests were always somewhat lower than those obtained in compression tests because of deformation occurring outside the gage length region; therefore, the moduli obtained from the compression tests were used for comparison at the different pressures and the moduli in tension were assumed to be the same as those in compression at each pressure, as was observed at atmospheric pressure.

The stresses and strains reported for specimens tested under superimposed hydrostatic pressure have been corrected for the effect of compressibility on specimen diameter and gage length at the different pressures. 22,23)

Experimental Results

Strength-Differential Effect

To obtain an accurate determination of the S-D effect at atmospheric pressure, where S-D = $2(|\sigma_{\rm c}| - |\sigma_{\rm t}|)/(|\sigma_{\rm c}| + |\sigma_{\rm t}|)$ and the subscripts c and t refer to compression and tension, respectively, several specimens of each polymer were tested in

tension and compression with a clip on strain gage used to measure length changes. These results are shown in Figures 1 and 2 for polyethylene and polycarbonate, respectively. The magnitude of the S-D effect is 5 ± 1 percent for polyethylene up to plastic strains of about 5 percent, after which it increases because of the different work-hardening behavior for tensile and compressive deformation. For polycarbonate, the magnitude of the S-D effect is 14 ± 2 percent for plastic strains up to the maximum point, after which it varies because necking and barreling of the tension and compression specimens occur, making length changes inaccurate for determining stresses and strains. Our results for the magnitudes of the S-D effect in polyethylene and polycarbonate are in agreement with previous work, which showed an S-D of about 13 percent in polycarbonate when the maximum points in the true-stresstrue-strain curves for tension and compression tests were used 24) and an S-D of about 6 percent in high-density polyethylene in the initial plastic strain region. 25) The actual values of the S-D appeared to increase with strain from the lower limits to the upper limits of the reported values for both polymers. As will be discussed in the hydrostatic-pressure-test results, this appears to be a real effect and not experimental variation.

The values obtained for the initial modulus of polyethylene and polycarbonate at atmospheric pressure were 1140 and 2350 MPa (165 and 341 ksi), respectively. These values for the initial modulus are at the high end of the range of values reported for these materials. 26)

Effect of Hydrostatic Pressure on Deformation

Tests on polyethylene and polycarbonate specimens pressurized at 1104 MPa for 15 minutes prior to testing at atmospheric pressure showed that pressurization itself did not change the deformation characteristics of these polymers. In addition, tests at atmospheric pressure in which both length change and diameter changes were used to calculate true stresses and true strains showed that both methods gave identical curves to strains just beyond the maximum load points in the tension tests, which is the strain region of most concern to this study.

The effects of hydrostatic pressure on the deformation behavior of polyethylene deformed in tension and compression are shown in Figures 3 and 4, respectively, plotted as engineering-stress—engineering-strain curves. These curves are the average of at least two specimens. As observed by others, 5,15,27) initial modulus and yield and flow stresses increase with increasing hydrostatic pressure. Because of space limitations in the hydrostatic-pressure unit the polyethylene specimens could not be fractured in tension. The crosses on the curves in Figure 3 indicate the strains at

which the specimens were unloaded, taken out of the pressure chamber, and recoated; an extension adaptor was then inserted in the specimen holder to allow additional extension after repressurization.

deformation behavior of polyethylene indicated that there was a change in the deformation mode from cold drawing to localized unstable necking, and therefore, a large decrease in the amount of plastic deformation under pressure. In the present study no change in deformation mode was observed at the different pressures, and the mode of deformation was typical of that observed at atmospheric pressure in air; that is, a necked region formed during the drop in load and this region propagated at relatively constant load until the test was terminated. The earlier observations on the change in deformation mode with pressure have been shown to be a consequence of an interaction between the pressure medium and the polyethylene. 15)

Figures 5 and 6 show the polyethylene specimens tested at the various pressures after the first unloading and after final termination of the test, respectively. The only apparent difference between the specimens is that the draw ratio is reduced at the higher pressures, which is similar to what is observed at lower temperatures. ²⁸⁾ Multiple necks form on reloading, especially at the higher pressures. At

1104 MPa the RTV silicone rubber coating became brittle and was split apart prior to both the first and second removals of the specimen from the pressure unit. However, the contact of the polyethylene with the pressure environment did not affect the deformation mode.

Examination of the polyethylene samples after deformation at atmospheric pressure and after deformation under hydrostatic pressure showed that stress whitening in the necked region was suppressed when deformation took place under hydrostatic pressure. This is a common observation in crystalline polymers and is believed to be a consequence of reduced void formation when deformation is performed under hydrostatic pressure. 4)

Figures 7 and 8 show the effects of hydrostatic pressure on the deformation behavior of polycarbonate deformed in tension and in compression, respectively, plotted as engineering-stress—engineering-strain curves. As reported previously, 5,29,30) the initial modulus and yield and flow stresses increase with increasing pressure. The specimens tested in the hydrostatic-pressure environment showed deformation behavior similar to that observed at atmospheric pressure in air.

After the peak stress was reached a neck formed, and this neck propagated along the gage length with final fracture occurring after the neck had propagated the entire gage length.

The only exception was at 1104 MPa where the brittleness of the RTV silicone rubber coating resulted in its fracturing
after about 40 percent elongation, which allowed the pressure
environment to come in contact with the polycarbonate so
that fracture resulted. When the test was stopped and the
specimen was removed, recoated, and subsequently repressurized
before testing continued, additional elongation occurred
beyond that at which fracture occurred in a sample that was
not recoated, indicating that the inability to protect the
polycarbonate specimens from the pressure environment was
probably the cause of the reduced elongation at 1104 MPa.

This type of procedure was used at most of the pressures, and the elongations obtained under pressure in these tests were similar to that obtained at atmospheric pressure in air. The samples deformed at 828 and at 1104 MPa had smaller gage lengths and diameters than the samples deformed at the other pressures, and this is the reason for the greater elongation before fracture at 828 MPa without recoating the specimen. As observed for polyethylene the draw ratio in polycarbonate decreased with increasing hydrostatic pressure.

Figures 9 and 10 show the tension and compression curves of polyethylene and polycarbonate, respectively, plotted as true-stress—true-strain curves. An S-D effect is apparent for both polymers at all the pressures' its magnitude appears

to be independent of pressure and is about 6 ± 1 and 13 ± 1 percent for polyethylene and polycarbonate, respectively, in the region near the initial deviation from linearity. It appears to increase slightly for both polymers to about 7.5 ± 1 and 16 ± 2 percent with strain, up to strains near the maximum stress in the tension specimens that show a maximum value. Pressure significantly changes the stress-strain behavior of these polymers. In polyethylene the initiation of necking, and therefore the maximum in the tensile stress-strain curve, occurs at lower strains, whereas the compression curves develop a plateau with increasing pressure (Figure 9). In polycarbonate both tension and compression tests change from showing strain-softening behavior to showing a continuous parabolic curve with increasing pressure (Figure 10).

The magnitudes obtained for the S-D effect in the Harwood unit are in reasonable agreement with those measured at atmospheric pressure by using a strain gage extensometer, 5 ± 1 and 14 ± 2 percent for polyethylene and polycarbonate, respectively. As discussed previously, the values at atmospheric pressure also appeared to increase with strain in the strain region just beyond the proportional limit. The slightly greater range for the S-D values obtained from testing in the Harwood unit is most likely a result of averaging all the values at the different pressures at a particular strain since the S-D effect appeared independent of pressure.

The effect of hydrostatic pressure on the slope of the initial linear region of the true-stress—true-strain curves (initial modulus) is shown in Figure 11. The relation for both polymers appears to be linear over the pressure range studied and shows the larger pressure dependence of the modulus of polyethylene as compared with polycarbonate, as has been indicated previously. The bars on the data points reflect small specimen variations, but more importantly, the possible variations in drawing the straight lines through the data points in the linear regions after machine displacements were eliminated from the total displacements measured, as discussed previously.

The polycarbonate results given in Figure 11 for the initial moduli at 138, 276 and 552 MPa are in good agreement with similar previous measurements up to pressures of 690 MPa (100 ksi) on this polymer. (100 ksi) The data for polyethylene show a more pronounced linearity with pressure than observed previously at pressures up to 690 MPa. The values reported here are lower at 138 and 276 MPa but much the same as the previous values at 552 MPa.

Volume Changes

The permanent volume changes remaining after plastic deformation of polyethylene and polycarbonate in tension and compression are shown in Figure 12. The results are similar

for tension and compression tests and show that polyethylene undergoes a permanent volume expansion, whereas polycarbonate undergoes a permanent volume contraction. The degree of expansion observed for polyethylene is similar to that observed previously for steels. 8,9) Therefore, these expansions, as well as those observed in the steels, are much smaller than those predicted from the normality flow rule of plasticity theory when the S-D effect is a result of pressure dependence of the yield and flow stresses. 31) However, the volume contractions resulting from plastic deformation of polycarbonate have not been observed in metals and are in qualitative as well as quantitative contrast to the normality flow rule, which requires a permanent volume expansion in a material showing pressuredependent yielding. 31)

Because of the significance of the observation of permanent volume contraction resulting from plastic deformation of polycarbonate, several specimens of each polymer were deformed in a dilatometer so that volume changes occurring during and subsequent to straining could be measured. Although the density measurements appeared reliable, there was the possibility that the liquid medium used for the measurements might have attacked the polymers, even though there was no evidence of this.

The results of the dilatometer measurements are shown in Figures 13 and 14 for polyethylene and polycarbonate, respectively. These results are in accord with the density measurements, showing that polyethylene undergoes a volume expansion whereas polycarbonate undergoes a volume contraction during plastic deformation. The permanent volume changes remaining after testing and unloading are similar to those determined from the density measurements. The dilatometer results also show tha the plastic volume change that occurs during deformation, given by the difference in the total volume contraction and the expected elastic volume contraction (extrapolation of the data in elastic region), is similar in magnitude to the permanent volume change remaining on unloading. The results obtained for polycarbonate (Figure 14) are in good agreement with some previously reported data for this polymer. 12) The values obtained for Poisson's ratio from the slope of the linear region of the curves in Figures 13 and 14 for polyethylene and polycarbonate were 0.31 and 0.36, respectively. These values appear in accord with those reported in the literature. 5)

Additional density measurements were made on compression specimens of each polymer which were deformed at
828 MPa. These results are included in Figure 12 and appear
similar to those obtained at atmospheric pressure.

Implications for Constitutive Models

Initial Modulus

As illustrated in Figure 11, the data for the initial modulus, E, in both polymers at the various pressures, p, fit the linear equation,

$$E = E_0 + mp$$
 (1)

where E is the modulus at zero pressure. The empirical values of m for polyethylene and polycarbonate were 5 and 3, respectively.

It has been suggested 27 that the pressure-dependent modulus is a consequence of nonlinear elastic behavior at the finite strains encountered when the applied pressure is a significant fraction of the modulus value. This is the case in these experiments on polymers, but not in the earlier experiments on metals. For Murnaghan's nonlinear elastic theory 32,33 this argument leads to Equation 1 with $m = 2(5-4v_0)(1-v_0)$ where v_0 is Poisson's ratio at zero pressure. Using the values 0.31 and 0.36 obtained for Poisson's ratio in polyethylene and in polycarbonate then gives values of m of 5.2 and 4.6, respectively. Thus, the calculated value for polyethylene is similar to the observed value, whereas that for polycarbonate is about 50 percent greater than the observed value.

For later comparison with the pressure dependence of flow stress, Equation 1 is rewritten as

$$E = (1 + \frac{m}{E_O} P) E_O = (1 + \alpha P) E_O$$
 (2)

where $P = -(\sigma_1 + \sigma_2 + \sigma_3)/3$ is the mean pressure, and is equal to the applied pressure for the initial modulus. The observed values of m, E_0 , and β are respectively 5, 1140 MPa, and 4.4 x 10^{-3} /MPa for polyethylene and 3, 2400 MPa, and 1.25 x 10^{-3} /MPa for polycarbonate.

Yield Conditions and S-D Effect

It was pointed out previously 8,9 that the yield condition for isotropic materials can always be expressed as a function of the three stress invariants, I_1 , I_2 , and I_3 where

$$I_{1} = \sigma_{1} + \sigma_{2} + \sigma_{3}$$

$$I_{2} = [3/2(\sigma_{1}^{'2} + \sigma_{2}^{'2} + \sigma_{3}^{'2})]^{1/2}$$

and

$$I_3 = [9/2(\sigma_1^3 + \sigma_2^3 + \sigma_3^3)]^{1/3}$$

In these equations σ_1 , σ_2 and σ_3 are the principal stresses and σ_1' , σ_2' and σ_3' are the principal deviator stresses given by

$$\sigma_{i}^{*} = \sigma_{i} - \frac{I_{1}}{3}$$

In the case of simple tension or compression under hydrostatic pressure, $I_1 = \sigma - 3p$, $I_2 = \pm \sigma$, and $I_3 = \sigma$. In these equations, σ is the flow stress taken as positive in tension and p is the hydrostatic pressure. The sign of I_2 must be taken so as to

make the resultant value positive; that is, + for tension, - for compression; on the other hand, I₃ is positive in tension and negative in compression.

For steels it has been shown⁹⁾ that the stresses at particular offset strains in tension and compression tests under hydrostatic pressure are well-represented by the linear yield function

$$I_2 + aI_1 + bI_3 = c$$
 (3)

In fact, the term involving I₃ was generally insignificant. To test this same yield function for polymers, a, b, and c were determined by a regression analysis of the stresses for polycarbonate and for polyethylene at the proportional limit and at one percent offset strains. The results are shown in Table I and in Figures 15 and 16. A good fit was obtained to the linear yield function for both polymers. For polycarbonate the compression and the tension data yielded different straight lines reflecting a significant role for the coefficient b, in contrast to the earlier results on steels. For polyethylene, the compression and tension data gave common lines reflecting an insignificant role for b, similar to the behavior observed earlier in steels. Both a and c were strain-dependent in the polymers, whereas the strain dependence of a was not so clear in the earlier results on steels. The strain dependence of a

also is in contrast with Argon's theory of deformation in glassy polymers. 34)

Substituting the values of the stress invariants into the yield condition, Equation 3, gives the following result for the dependence of the flow stress, σ , on the mean pressure $P = -I_1/3$,

$$\sigma = (1 + \frac{3a}{c} P) \sigma_{0} = (1 + \alpha' P) \sigma_{0}$$
 (4)

where $\sigma_{_{O}}$ is the flow stress at zero pressure and is different for tension and compression in polycarbonate. Using the a and c values in Table I shows that α is strain independent and its value is about 4.9 x 10^{-3} /MPa and 1.0 x 10^{-3} /MPa for polyethylene and polycarbonate, respectively. These values for α ' are essentially the same as those for α (4.4 x 10^{-3} /MPa and 1.25 x 10^{-3} /MPa for polyethylene and polycarbonate, respectively) computed for the initial modulus. This demonstrates that the pressure dependence of flow stress is essentially the same as the pressure dependence of the initial modulus in the polymers tested. Such similar dependence has been suggested previously 4 , 5) but does not seem to have been so unequivocally demonstrated.

For the yield condition given by Equation 3, the magnitude of the S-D effect is given by $^{8)}$

$$S-D = 2(a+b)$$
 (5)

For the values of a and b shown in Table I, the predicted values of S-D are shown along with the observed values, and the agreement is seen to be good.

Flow Rule

It was pointed out previously ^{8,9)} that the most commonly accepted flow rule in plasticity theory, the normality flow rule, ³¹⁾ requires that any material with pressure-dependent yielding must exhibit volume expansion with deformation. For the yield condition given by Equation 3, the ratio of permanent volume expansion to axial strain is given by

$$\gamma = \frac{3a}{1 \pm (a+b)} \tag{6}$$

where the + sign applies to tension and the - sign to compression. The values of γ predicted from this equation are listed in Table I along with the measured values, which were taken as the slopes of the straight lines in Figure 12. The calculated values are the average for tension and compression but the smallness of the (a+b) term with respect to 1 makes the predicted expansions similar for tension and compression.

Although the magnitude of the predicted volume expansion for polyethylene is much larger than that observed, as was the case in steels, 8,9) the volume contraction with plastic deformation of polycarbonate is in contradiction to the normality flow rule of plasticity theory.

These results suggest a constitutive model for polymers in which the flow stress is linearly dependent on mean pressure, but in which inelastic volume change is negligible, in agreement with earlier findings for steels. 8,9) The results also suggest, however, that the pressure dependence of flow stress in polymers is the same as that of the initial modulus, which is not true for steels.

Conclusions

- 1. The pressure dependence of flow stress in polyethylene and polycarbonate is linear, and is essentially the same as the pressure dependence of the initial modulus.
- 2. The S-D effect in polyethylene is primarily a manifestation of the pressure-dependent flow stress; that in polycarbonate involves other factors such as anisotropy or dependence of flow on the third stress invariant.
- 3. The inelastic volume change is positive in polyethylene and negative in polycarbonate and much smaller in magnitude than that required by the normality flow rule.
 - 4. Pressure inhibits strain softening in polycarbonate.
- Pressure inhibits tensile necking in polycarbonate,
 but promotes its initiation in polyethylene.
- 6. Pressure does not inhibit cold drawing of the polymers, but it does reduce the draw ratio in both polyethylene and polycarbonate.

Acknowledgement

The authors gratefully acknowledge helpful discussions with R. D. Hoffman and L. Anand, and the assistance of R. J. Sober with the experiments and H. L. Morrison with data analysis.

References

- R. M. Caddell, R. S. Raghava, and A. G. Atkins, "Pressure Dependent Yield Criteria for Polymers," Materials Science and Engineering 13, 113 (1974).
- I. M. Ward, "Review: The Yield Behavior of Polymers," Journal of Materials Science 6, 1397 (1971).
- 3. R. G. C. Arridge, <u>Mechanics of Polymers</u>, Chapter 7, Clarendon Press, Oxford (1975).
- 4. J. A. Sauer, "Deformation, Yield and Fracture of Polymers at High Pressure," Polymer Engineering and Science 17, 150 (1977).
- K. D. Pae and S. K. Bhateja, "The Effects of Hydrostatic Pressure on the Mechanical Behavior of Polymers," Journal of Macromolecular Science - Reviews in Macromolecular Chemistry C13, 1 (1975).
- E. Jones Parry and D. Tabor, "Review Effect of Hydrostatic Pressure in the Mechanical Properties of Polymers: A Brief Review of Published Data," Journal of Materials Science 8, 1510 (1973).
- 7. S. V. Radcliffe, "Effects of Hydrostatic Pressure on the Deformation and Fracture of Polymers," <u>Deformation and</u> Fracture of High Polymers, Plenum Press, New York (1973).
- 8. W. A. Spitzig, R. J. Sober, and O. Richmond, "Pressure Dependence of Yielding and Associated Volume Expansion in Tempered Martensite," Acta Metallurgica 23, 885 (1975).
- 9. W. A. Spitzig, R. J. Sober, and O. Richmond, "The Effect of Hydrostatic Pressure on the Deformation Behavior of Maraging and HY-80 Steels and its Implications for Plasticity Theory," Metallurgical Transactions 7A, 1703 (1976).
- A. J. M. Spencer, "A Theory of the Kinematics of Ideal Soils Under Plane Strain Conditions," 12, 337 (1964).
- H. L. Morrison and O. Richmond, "Application of Spencer's Ideal Soil Model to Granular Materials Flow," Journal of Applied Mechanics 98, 49 (1976).

- C. A. Pampillo and L. A. Davis, "Volume Change During Deformation and Pressure Dependence of Yield Stress," Journal of Applied Physics 42, 4674 (1971).
- 13. J. A. Harris, I. M. Ward, and J. S. C. Parry, "Shear Strength of Polymers Under Hydrostatic Pressure: Surface Coatings Prevent Premature Fracture," Journal of Materials Science 6, 110 (1971).
- 14. K. Matsushige, S. V. Radcliffe, and E. Baer, "The Mechanical Behavior of Polystyrene Under Pressure," Journal of Materials Science 10, 833 (1975).
- 15. S. Kapur and E. Baer, "The Effect of the Environment on the Mechanical Behavior of Semi-Crystalline Polymers at High Pressures," Technical Report No. 5, Office of Naval Research, Contract N00014-75-C-0795, November 10, 1976.
- 16. G. C. Rauch and W. C. Leslie, "The Extent and Nature of the Strength-Differential Effect in Steels," Metallurgical Transactions 3, 373 (1972).
- 17. F. Garofalo and H. A. Wriedt, "Density Change in an Austenitic Stainless Steel Deformed in Tension and Compression," Acta Metallurgica 10, 1007 (1962).
- 18. H. Ll. D. Pugh, "The Mechanical Properties and Deformation Characteristics of Metals and Alloys Under Pressure,"

 Irreversible Effects of High Pressure and Temperature on Materials, p. 68, ASTM STP No. 374 (1965).
- 19. J. E. Hanafee and S. V. Radcliffe, "Effect of High Pressure on a Strain Gauge Load Cell," The Review of Scientific Instruments 38, 328 (1967).
- 20. A. Oguchi and S. Yoshida, "A Magnetostrictive Load Cell for Use Under High Hydrostatic Pressures," Japanese Journal of Applied Physics 7, 672 (1968).
- 21. E. O. Hall, <u>Yield Point Phenomena in Metals and Alloys</u>, Chapter 1, Plenum Press, New York (1970).
- 22. R. W. Warfield, "Compressibility of Linear Polymers," Journal of Applied Chemistry 17, 263 (1967).

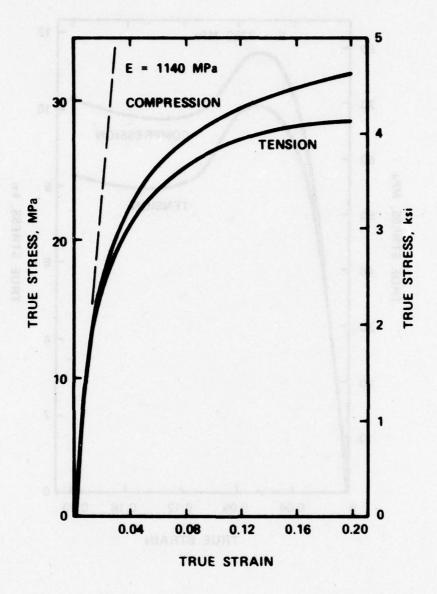
- 23. D. J. Pastine, "P,v,T Equation of State for Polyethylene,"
 The Journal of Chemical Physics 49, 3012 (1968).
- 24. C. Bauwens-Crowet, J. C. Bauwens, and G. Homes, "The Temperature Dependence of Yield of Polycarbonate in Uniaxial Compression and Tensile Tests," Journal of Materials Science 7, 1976 (1972).
- 25. N. Ibrahim, D. M. Shinozaki and C. M. Sargent, "Deformation Resistance and the Flow Curve in High-Density Polyethylene," Materials Science and Engineering 30, 175 (1977).
- 26. Polymer Handbook, J. Brandrup and E. H. Immergut, editors, 2nd Edition, Chapter VIII, John Wiley and Sons, New York (1975).
- 27. D. R. Mears, K. D. Pae, and J. A. Sauer, "Effects of Hydrostatic Pressure on the Mechanical Behavior of Polyethylene and Polypropylene," Journal of Applied Physics 40, 4229 (1969).
- 28. Y. Wada, "Necking of High-Density Polyethylene," Journal of Applied Polymer Science 15, 183 (1971).
- 29. J. A. Sauer, D. R. Mears, and K. D. Pae, "Effects of Hydrostatic Pressure on the Mechanical Behavior of Polytetrafluoethylene and Polycarbonate," European Polymer Journal 6, 1015 (1970).
- 30. A. W. Christiansen, E. Baer and S. V. Radcliffe, "The Mechanical Behavior of Polymers Under High Pressure," Philosophical Magazine 24, 451 (1971).
- 31. D. C. Drucker, "A More Fundamental Approach to Plastic Stress-Strain Relations," Proceedings 1st U. S. National Congress Applied Mechanics, 487 (1952).
- F. D. Murnaghan, "Finite Deformation of an Elastic Solid," American Journal of Mathematics 59, 235 (1937).
- 33. F. Birch, "The Effect of Pressure Upon the Elastic Parameters of Isotropic Solids, According to Murnaghan's Theory of Finite Strain," Journal of Applied Physics 9, 279 (1938).
- A. S. Argon, "A Theory for the Low-Temperature Plastic Deformation of Glassy Polymers," Philosophical Magazine 28, 839 (1973).

Table I

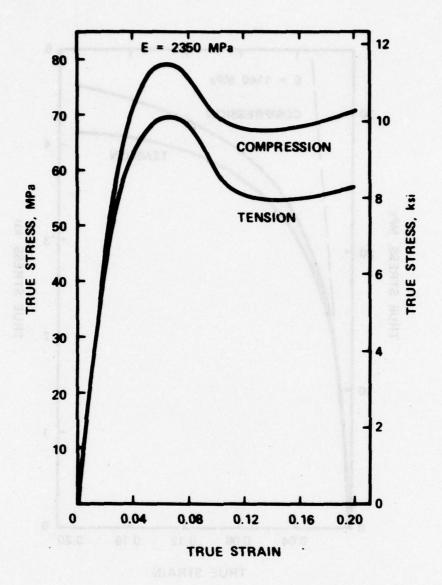
Comparison of the Experimental and Predicted Values for the Strength Differential (S-D) and Volume Expansion γ During Yielding

7	Observed Predicted	0.011 0.066	960.0	-0.025 0.033	0.067
				-0-	
040	Observed Predicted	0.9	8.	13.0	17.4
S-D,	Observed	6±1	7.5±1	13±1	16±2
	b* c*, MPa	13.0	19.6	36.0	66.5
	*0	0.022 0.008 13.0	0.032 0.012 19.6	0.011 0.054 36.0	0.022 0.065 66.5
	*	0.022	0.032	0.011	0.022
	Strain	Proportional Limit	1% Offset	Proportional Limit	1% Offset
	Polymer	Polyethylene		Polycarbonate	

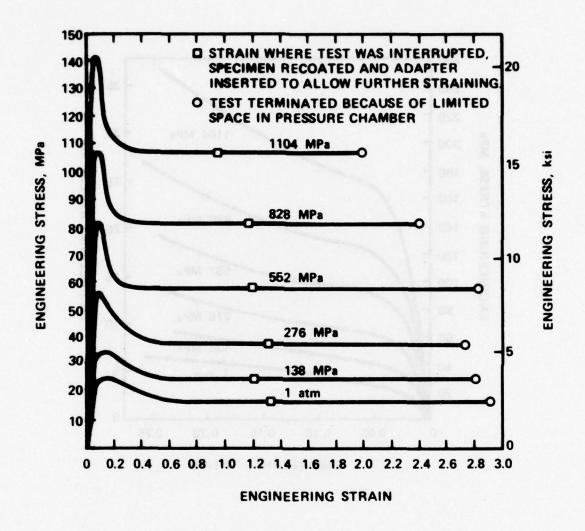
^{*} Coefficients in Eq. I_2 + aI_1 + bI_3 = c



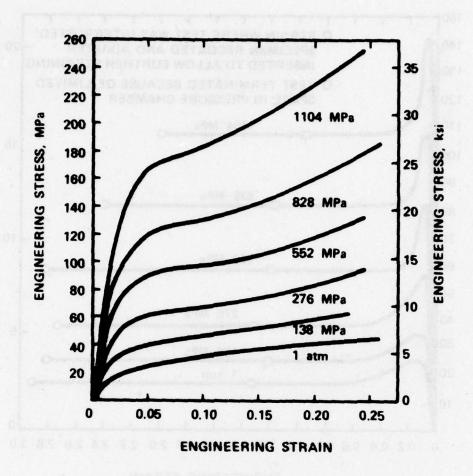
TRUE-STRESS—TRUE-STRAIN CURVES IN TENSION AND IN COMPRESSION FOR POLYETHYLENE OBTAINED FROM COMBINED TENSION-COMPRESSION SPECIMENS



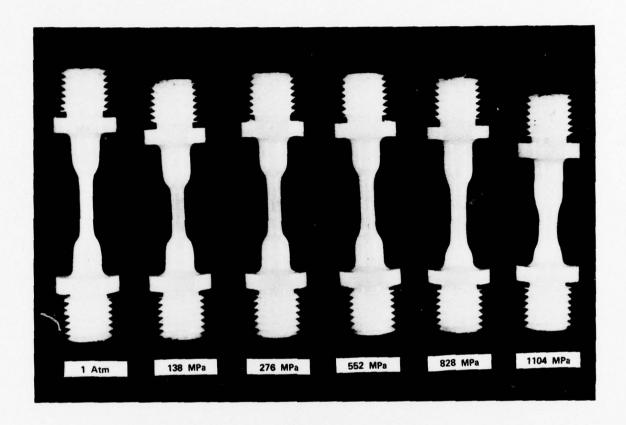
TRUE-STRESS-TRUE-STRAIN CURVES IN TENSION AND IN COMPRESSION FOR POLYCARBONATE OBTAINED FROM COMBINED TENSION-COMPRESSION SPECIMENS



EFFECT OF HYDROSTATIC PRESSURE ON THE TENSILE ENGINEERING STRESS-ENGINEERING-STRAIN CURVES OF POLYETHYLENE



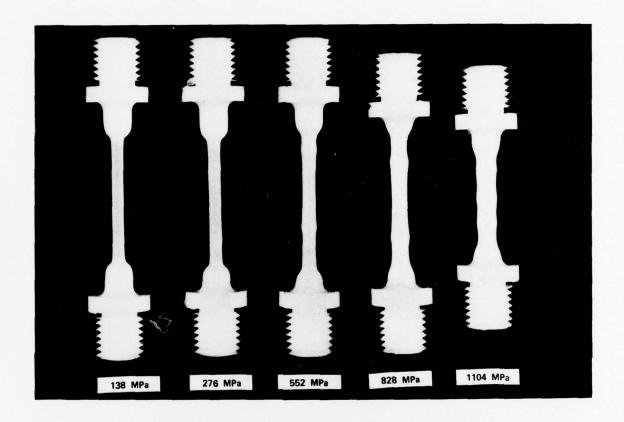
EFFECT OF HYDROSTATIC PRESSURE ON THE COMPRESSIVE ENGINEERING-STRESS—ENGINEERING-STRAIN CURVES OF POLYETHYLENE



Tension specimens of polyethylene after deformation to the strain where the test was interrupted, specimen recoated, and adapter inserted to allow further straining.

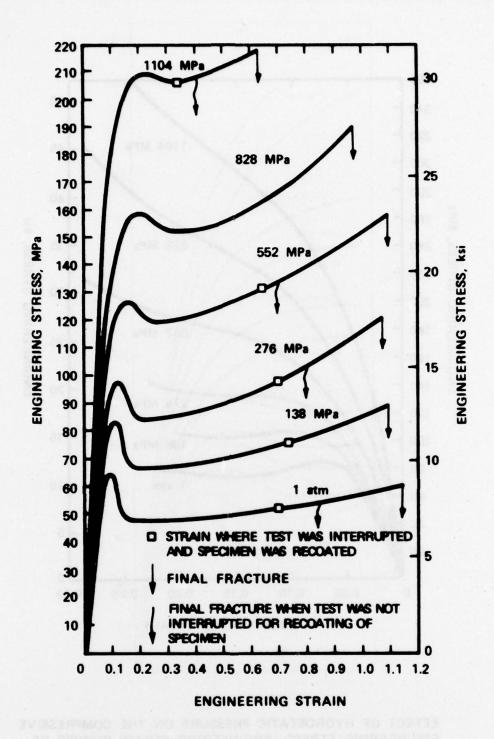
P-7138B-2

Figure 5.

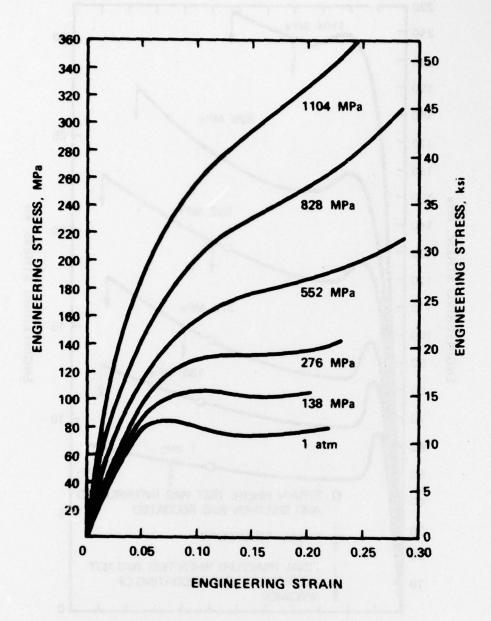


Tension specimens of polyethylene after repressurization and continued deformation to the maximum amount of extension available in the pressure chamber.

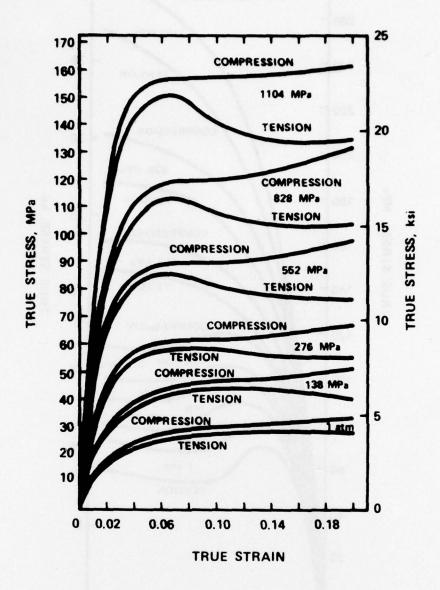
P-7138B-1 Figure 6.



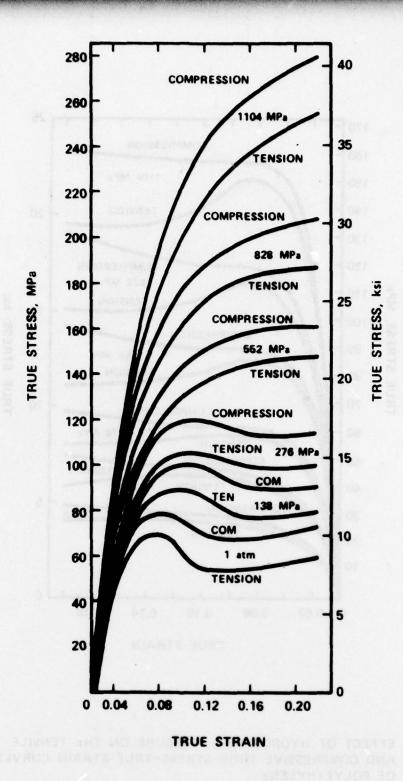
EFFECT OF HYDROSTATIC PRESSURE ON THE TENSILE ENGINEERING-STRESS—ENGINEERING STRAIN CURVES OF POLYCARBONATE



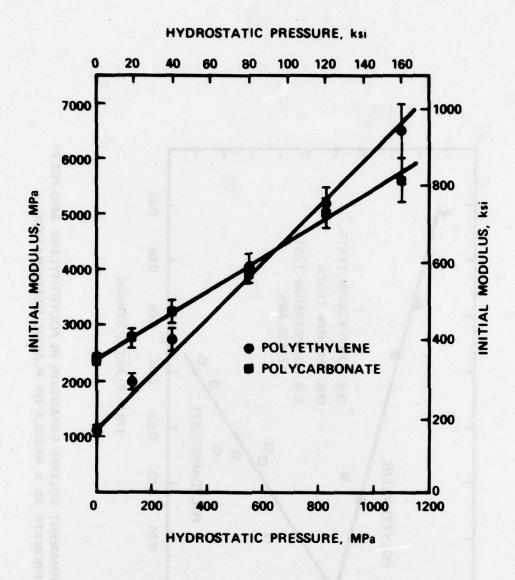
EFFECT OF HYDROSTATIC PRESSURE ON THE COMPRESSIVE ENGINEERING-STRESS—ENGINEERING-STRAIN CURVES OF POLYCARBONATE



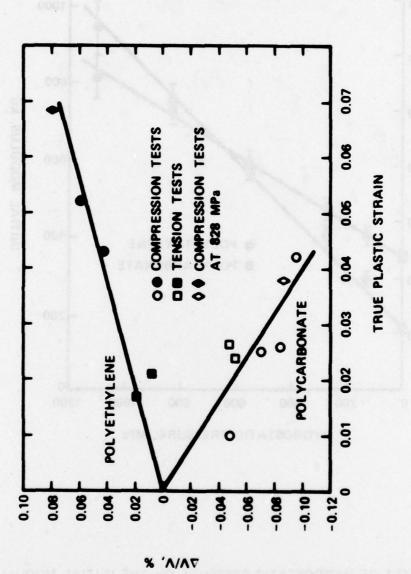
EFFECT OF HYDROSTATIC PRESSURE ON THE TENSILE AND COMPRESSIVE TRUE-STRESS-TRUE STRAIN CURVES OF POLYETHYLENE



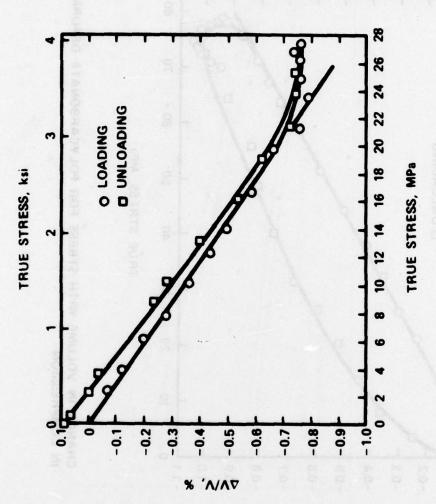
EFFECT OF HYDROSTATIC PRESSURE ON THE TENSILE AND COMPRESSIVE TRUE-STRESS-TRUE-STRAIN CURVES OF POLYCARBONATE



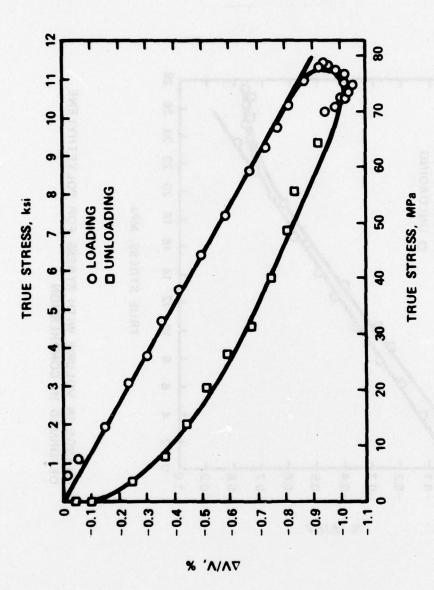
EFFECT OF HYDROSTATIC PRESSURE ON THE INITIAL MODULI OF POLYETHYLENE AND POLYCARBONATE



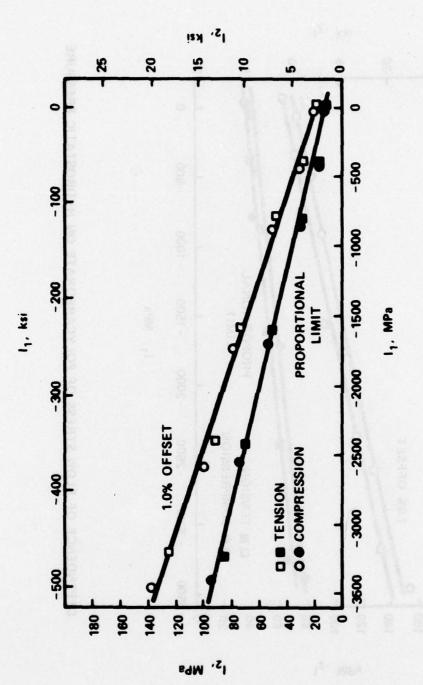
PERMANENT VOLUME EXPANSION IN POLYETHYLENE AND POLY-CARBONATE AS A RESULT OF PLASTIC DEFORMATION



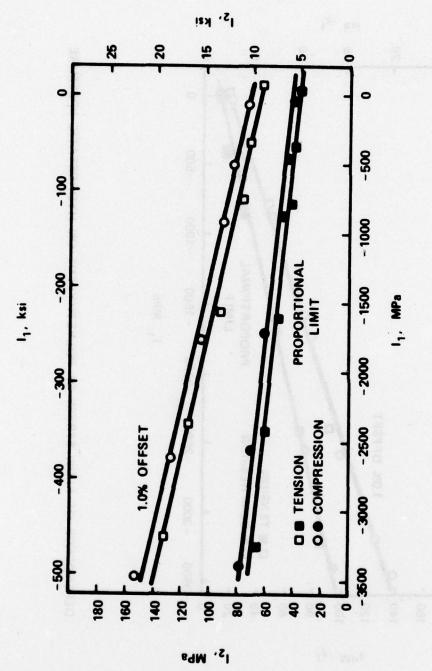
CHANGE IN VOLUME WITH STRESS FOR POLYETHYLENE DEFORMED IN COMPRESSION



CHANGE IN VOLUME WITH STRESS FOR POLYCARBONATE DEFORMED IN COMPRESSION



DEPENDENCE OF FLOW STRESS OF POLYETHYLENE ON HYDROSTATIC PRESSURE



DEPENDENCE OF FLOW STRESS OF POLYCARBONATE ON HYDROSTATIC PRESSURE

SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered) READ INSTRUCTIONS BEFORE COMPLETING FORM REPORT DOCUMENTATION PAGE I. REPORT NUMBER 2. GOYT ACCESSION NO. 3. RECIPIENT'S CATALOG NUMBER 5. TYPE OF REPORT & PERIOD COVERED Effect of Hydrostatic Pressure on the Deformation Behavior of Polyethylene and 1/77 - 5/31/78Polycarbonate in Tension and in Compression L)6-H-031 (061/066-1) W. A. Spitzig and O. Richmond 14-76-C-9. PERFORMING ORGANIZATION NAME AND ADDRESS PROGRAM ELEMENT, PROJECT, AREA & WORK UNIT NUMBERS United States Steel Corporation Research Laboratory, 125 Jamison Lane NR 039-133/5-04-77 (471) Monroeville, Pennsylvania 15146 12. REPORT DATE 11. CONTROLLING OFFICE NAME AND ADDRESS June 30, 1978 United States Steel Corporation Research Laboratory, 125 Jamison Lane Monroeville Penneylvania 15146
WONITORING AGENCY NAME CADDRESS(II dillerent from Controlling Office) 15. SECURITY CLASS. (of this report) Jun 78 Unclassified 15a. DECLASSIFICATION DOWNGRADING SCHEDULE 16. DISTRIBUTION STATEMENT (of this Report) Distribution of this document is unlimited. rept. I Jun 77-31 May 78, 18. SUPPLEMENTARY NOTES 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) stress-strain behavior plastic deformation polyethylene density determinations plasticity polycarbonate volume expansion compression deformation

The stress-strain response of crystalline high density polyethylene and of amorphous polycarbonate has been determined in tension and in compression at superimposed pressures up to 1104 MPs (160 ksi). All tests were conducted at room temperature and at a single imposed strain rate, and the specimens were coated with silicone rubber to protect them from the pressurizing fluid. Strain softening occurred in the polycarbonate at low pressures

DD , FORM , 1473

EDITION OF 1 NOV 45 IS OBSOLETE S/N 0102-014-6601

AH Unclassified

Unclassified

UNCLASSIFICATION OF THIS PAGE (When Date Entered)

but was inhibited by pressure. Tensile necking occurred in both materials, but was promoted by pressure in polyethylene and inhibited in polycarbonate.

The initial modulus, E, and the flow stress, σ , at a given offset strain varied linearly with the mean pressure, P, with essentially the same pressure coefficient, σ . Thus $E = (1+\alpha P)E_0$ and $\sigma = (1+\alpha P)\sigma_0$, where E_0 and σ_0 are values at zero mean pressure. In polyethylene, the coefficient, σ_0 , was the same in tension and compression, indicating that the strength differential between tension and compression was a simple manifestation of pressure-dependent yielding, as was found previously for steels. In polycarbonate the coefficient, σ_0 , was different in tension and in compression, implying an effect due to the third stress invariant or to anisotropy.

Inelastic volume changes were determined from density and from dilatometer measurements. In polyethylene they were positive but much less than required by the normality flow rule of plasticity theory. This is consistent with earlier results on steels. In polycarbonate they were negative, in complete contrast to predictions of the normality flow rule.

The results suggest a constitutive model for polymers in which the flow stress is linearly dependent on mean pressure, but in which inelastic volume change is negligible, in agreement with earlier findings for steels. The results also suggest, however, that the pressure dependence of flow stress in polymers is the same as that of the initial modulus, which is not the case with steels.